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Selective catalytic oxidation of benzyl alcohols to benzaldehydes with a dinuclear manganese(iv) complex

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A dinuclear manganese(IV) catalyst is capable of oxidising benzylic alcohols to benzaldehydes with very high turnovers numbers (up to 1000) and high selectivities (above 99%).

A key reaction in synthetic organic chemistry is the transformation of alcohols to aldehydes. Many procedures have been developed over the years, most notably the Oppenhauer and Swern oxidations and reactions utilising high valent metal compounds such as MnO_2, ammonium perruthenates and pyridinium chlorochromate.[1] However, almost all require stoichiometric amounts of metal compounds and sometimes co-oxidants, with concomitant environmental problems. Only a few examples are known in which metal complexes are used in a catalytic fashion. Benzaldehydes are obtained from benzyl alcohols with $RuCl_2(PPh_3)_3$[2] and $ZrO(OAc)_2$ using PhIO or *tert*-butyl hydroperoxide as oxidants,[3] and similar results were obtained with SeO_2–bis(4-anisyl) selenoxide.[4] A valuable alternative is the $[NBu_4][RuO_4]$–*N*-methylmorpholine oxide system.[5] These procedures typically require 1–10 mol% of catalyst and 100–300 mol% oxidant. Herein we report a novel method for the efficient and highly selective oxidation of benzylic alcohols to benzaldehydes using an active dinuclear manganese(iv) complex as catalyst and hydrogen peroxide or *tert*-butyl hydroperoxide as oxidant.

The excellent bleaching and epoxidation properties of **1** in water[6a] and acetone[6b,c] were recently reported. This complex consists of two manganese(iv) ions held together by three oxo ligands, with both metals bound to an *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane ligand.[7] The intriguing coordination chemistry of this ligand and its analogues has been reviewed.[8]

Initial results of the benzylic oxidation by using 0.6 μm **1**, 5 mm H_2O_2 and 0.6 mm benzyl alcohol in acetone in air were quite promising as highly selective aldehyde formation was observed, although the catalytic activity was modest (280 turnovers; entry 1, Table 1). Due to the efficient catalase activity of **1** under these conditions, we anticipated that excess of oxidant is required, but in attempting to increase the turnover number by using a very large excess hydrogen peroxide we only observed formation of benzoic acid (entry 2).‡ This could be overcome by adding 2000 equiv. of oxidant over a 10 h period, which cleanly gave 380 turnovers to benzaldehyde (entry 3). The mononuclear Mn^{III} complex **2** gives a somewhat higher conversion with benzyl alcohol, but the bis(μ-acetato)(μ-oxo) complex **3** was virtually unreactive (entries 4 and 5). Complexes such as **3** are most probably dead ends in the catalytic cycle when, starting with **1** or **2**, traces of benzoic acid are formed during the oxidation reaction. Indeed, addition of a few equivalents of benzoic acid with respect to **1** completely inhibits any turnover on benzylic alcohols when the reaction is carried out under nitrogen atmosphere (entry 6). Exposure to air eventually leads to full conversion to benzoic acid. For practical synthetic applications further improvements with complete conversion to benzaldehydes were highly desirable.

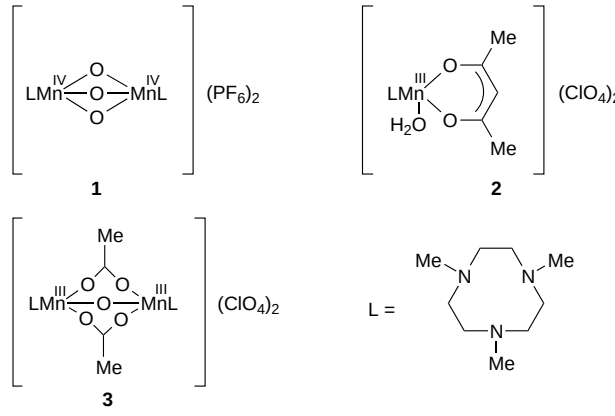

Table 1 Effects of changing various parameters on the reactivity of benzyl alcohol

Entry	Catalyst and oxidant[a]	Variation	Turnover[b]	*t*/min	Selectivity[c]
1	**1** + H_2O_2		280	100	> 99
2	**1** + H_2O_2 (80 000 equiv.)		1000	60	> 99[d]
3	**1**	[e]	380	600	> 99
4	**2**[f] + H_2O_2		660	100	> 99
5	**3**[g] + H_2O_2		16	60	> 99
6	**1** + H_2O_2	BnOH (2 equiv.) added	0	—	—
7	**1** + Bu^tO_2H		0	—	—
8	**1** + Bu^tO_2H	Pretreatment with H_2O_2	480	150	> 99
9	**1** + H_2O_2	Pretreatment with H_2O_2	360	150	> 99
10	H_2O_2	No catalyst added	0	—	—

[a] In all cases 1000 equiv. alcohol and 8000 equiv. oxidant were used in acetone in air; the reaction was followed by GC and terminated when conversion ceased to give benzaldehydes as product (the selectivity on aldehyde in all cases was above 99%). [b] Turnover number in mol aldehyde per mol **1**. [c] Selectivity in mol aldehyde per mol converted substrate. [d] Benzoic acid was the only product. [e] 2000 equiv. H_2O_2 in acetone were added over a 10 h period. [f] Ref. 9. [g] Ref. 7*b*.

Table 2 Reactivity of substituted benzyl alcohols using two different procedures

		Method A		Method B	
Entry	Substrate[a]	Turnover[b]	*t*/min	Turnover[b]	*t*/min
1	Benzyl alcohol	360	60	480	150
2	4-Methoxybenzyl alcohol	710	45	1000	45
3	3,4-Dimethoxybenzyl alcohol	300	60	1000	20
4	4-(Dimethylamino)benzyl alcohol	—		1000	20
5	4-Chlorobenzyl alcohol	700	45	1000	25
6	2-Chlorobenzyl alcohol	490	45	1000	40
7	2,6-Dichlorobenzyl alcohol	80	90	—	
8	4-Nitrobenzyl alcohol	530	15	1000	45
9	3-Nitrobenzyl alcohol	580	20	1000	25
10	2-Nitrobenzyl alcohol	240	15	1000	35
11	4-Trifluoromethylbenzyl alcohol	340	210	600	50
12	Octan-2-ol	360	100	360	90

[a] In all cases 1000 equiv. alcohol were used in acetone under inert atmosphere; the reaction was followed by GC and terminated when conversion ceased to give benzaldehydes as product (the selectivity on aldehyde in all cases was above 99%). [b] Turnover number in mol aldehyde per mol **1**.

To our surprise we found that the activity is significantly increased by employing a modified procedure. First the catalyst is mixed with 3000 equiv. of hydrogen peroxide in acetone for 30 min during which all hydrogen peroxide is decomposed (probably *via* catalase activity of **1**).§ Addition of an aliquot of substrate and hydrogen peroxide (1000 and 8000 equiv., respectively) to the thus pretreated catalyst leads to quantitative formation of benzoic acid, but under an inert atmosphere to selective formation of benzaldehyde (360 turnovers, entry 9). For substituted benzyl alcohols generally 400–700 turnovers to the corresponding benzaldehydes are found with over 99% selectivity with or without inert atmosphere conditions (Table 2, method A).

Although compound **1** with *tert*-butyl hydroperoxide (TBHP) is not active in the benzylic oxidation (Table 1, entry 7), the use of TBHP as oxidant in the second step, *i.e*. after pretreating **1** with hydrogen peroxide for 30 min, was found to have a highly beneficial influence on both turnover number and reaction rate (Table 1, entry 8). Nearly all substituted benzylic alcohols were fully converted to the corresponding benzaldehydes with excellent selectivities within an hour at room temperature using 0.1 mol% of catalyst **1** (Table 2, method B).¶

From the results with method A, we see a small but distinct steric effect as *ortho*-substituted substrates react more sluggishly than either *meta*- or *para*-substituted benzyl alcohols. In fact 2,6-disubstituted substrates are largely unreactive (entry 7). Substrates with electron-donating properties, *e.g*. (di)methoxy and dimethylamine benzyl alcohol (entries 2, 3 and 4), also appear to react faster under the conditions of method A than those with electron-withdrawing substituents such as nitro and trifluoromethyl groups (entries 8 and 11). The latter one even failed to give full conversion under the conditions of method B. As expected, secondary alcohols are selectively converted to ketones although the outcome is indifferent towards the procedure used. A typical example is given in entry 12.

In conclusion, we have demonstrated that manganese complex **1** is an excellent catalyst or catalyst precursor in novel procedures employing either H_2O_2 or TBHP as oxidant for the highly selective and very fast conversion of substituted benzyl alcohols to benzaldehydes. Further studies to elucidate the role of the pretreatment procedure and the exact nature of the catalytic species are in progress.

Footnotes

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‡ A control experiment showed that **1** is capable of oxidising benzaldehyde to benzoic acid in air. In 90 min, 125 turnovers were found in acetone, whereas a blank reaction, *i.e*. without **1**, gave no reaction at all. 3-Nitrobenzaldehyde is not oxidised by **1** in air, or by **1** and H_2O_2 under turnover conditions.

§ From the 16 line spectrum obtained from EPR measurements at 77 K we inferred that **1** is reduced to a dinuclear Mn^{III}–Mn^{IV} mixed valent species instantaneously when mixed with excess hydrogen peroxide in acetone, although we do not know if this reaction goes to full completion.[6a] Within 20 min the spectrum gradually changes to ultimately give a 6 line spectrum, indicative of Mn^{II} species.

¶ A general experimental procedure is as follows: 1.0 ml of a 0.6 mm stock solution of crystallised **1** in acetone and 0.5 ml of hydrogen peroxide (30 wt%) are mixed for 30 min at room temperature under a nitrogen atmosphere. Simultaneously 0.6 mmol substrate and 0.5 ml hydrogen peroxide (30 wt%) (method A) or 0.6 mmol substrate and 0.5 ml of aqueous *tert*-butyl hydroperoxide (70 wt%) (method B) are added and the reaction is followed by GC until the maximum conversion is reached (usually within 1 h).

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